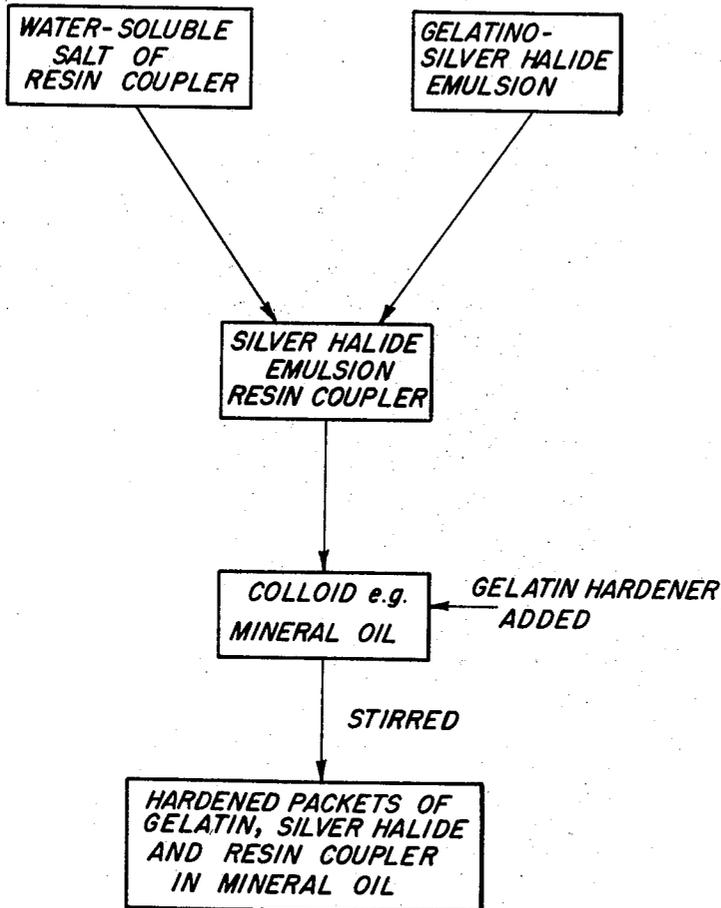


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PREPARATION OF PHOTOGRAPHIC PACKET EMULSIONS
BY A WATER-IN-OIL SYSTEM
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PREPARATION OF PHOTOGRAPHIC PACKET EMULSIONS BY A WATER-IN-OIL SYSTEM

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5 Claims. (Cl. 96—97)

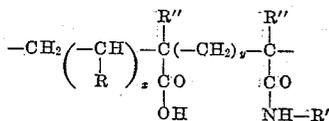
This invention relates to color photography and particularly to mixed packet photographic emulsions.

Prior suggestions for making mixed packet photographic emulsions have included many ways of forming the packets. One of these ways is described in Godowsky and Minsk U. S. Patent 2,698,797 in which a dispersion of packets is produced by the interaction of the gelatin of a gelatino-silver halide emulsion, and a resin coupler combination, in the presence of either a water-soluble polymer containing salt-forming acid groups or a precipitant of such polymer.

We have now found that photographic emulsion packets may be prepared by mixing a gelatino-silver halide emulsion with a resin coupler of the composition defined below or other non-diffusing, water-soluble coupler, and dispersing this emulsion-containing coupler in an oily or hydrophobic liquid, hardening the emulsion particles while in finely dispersed form in the oily liquid and then removing the hardened packets and redispersing them, together with other similarly formed packets, if desired, in plain gelatin or other hydrophilic colloid.

The accompanying drawing is a flow sheet illustrating the steps in our process.

The resin couplers which we propose to use have the following recurring structure:



where R is hydrogen or a phenyl, alkyl, alkoxy, carboxy-alkyl or acyloxy radical, x and y are 0 or 1, R' represents a color-forming group capable of reacting with the oxidation product of a primary aromatic amino developing agent on photographic development, and R'' is hydrogen or an alkyl radical, e. g., methyl or ethyl, said color-forming material containing an aryl group.

According to our invention, a solution of the sodium salt or other water-soluble salt of the resin-coupler is added to the silver halide emulsion and a solution of the resin coupler in the silver halide emulsion formed as shown in the three boxes at the top of the drawing. This emulsion is then added to a viscous hydrocarbon oil, for example, mineral oil containing diglycerol monolaurate as a dispersing agent, a gelatin hardener added to the mixture and the mixture stirred until finely dispersed hardened particles of gelatin, silver halide and resin coupler in the mineral oil or other oily liquid are obtained. The hardened particles or packets are then filtered or otherwise removed from the dispersion and redispersed in gelatin. This dispersion can then be coated as a single packet emulsion layer or another similarly formed dispersion can be added to it and coated as a mixed packet layer.

Mechanical means are preferably employed in bringing about the water-in-oil dispersion. Other methods may, however, be employed such as projection through

orifices, spinning or vibrating in the oil phase, ultrasonic vibration, various forms of colloid mills, etc.

The hydrophobic colloid or oily liquid may be mineral oil, e. g. Nujol, other viscous hydrocarbon oils, tricresyl-phosphate, etc. Suitable dispersing agents are preferably employed in the oily liquid. Glycerol monolaurate is especially suited for mineral oil. Other hydrophobic liquids such as a solution of dammar resin in xylene may be used.

In addition to the resin couplers, other non-diffusing, water-soluble couplers may be employed, as shown in Example 5.

The formation of the packet emulsions will be described in the following examples:

Example 1

One gram of a resin coupler of Example 12 of U. S. Patent 2,698,797 was dissolved in a solution of 7 cc. of 0.5 N sodium hydroxide and 10 cc. of distilled water.

This solution was added to 100 grams of a red-sensitive silver bromoiodide emulsion at 40° C. The pH of the emulsion was then adjusted to 6.06 at 40° C. with aqueous citric acid. The total weight was then 124 grams.

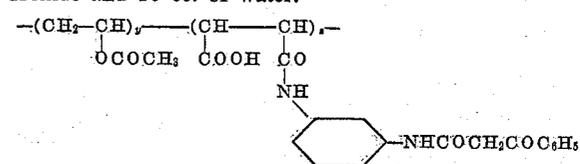
To 200 cc. of mineral oil (Nujol) in a one-liter beaker immersed in a water bath at 45° C. and stirred in a mixer with a 2" propeller was added dicresyl monolaurate in an amount of 2% based on the weight of oil. To this was added 25 cc. of the above emulsion at 40° C. and the mixture was stirred for ten minutes. Two cc. of a 5% aqueous solution of mucochloric acid was added at 40° C. and stirring was continued overnight while the bath temperature was permitted to drop spontaneously to room temperature (the bath dropped to room temperature in about 2 hours). After about 15 hours the mixture was chilled by placing ice and water in the bath and maintained at 10° or lower for 15 minutes.

Throughout the following operations all liquids were cooled to 10° or less before addition and the beaker and contents were kept in an ice bath. Five hundred cc. of petroleum ether were then added slowly with continued stirring. Immediately after the addition of the petroleum ether the propeller was changed to a 1½" size, and the mixture was stirred for 2 minutes. The stirrer was then removed and the packets allowed to settle.

When the packets had settled to the bottom the supernatant liquid was poured off and 500 cc. of fresh petroleum ether was added with stirring and the stirring, settling and decanting process repeated. One hundred cc. of petroleum ether was then added and after stirring, 500 cc. of absolute alcohol was poured in over a period of about 30 seconds. The suspension was stirred for 5 minutes and the packets were filtered onto a Buchner funnel. They were washed on the funnel with fresh portions of alcohol. The packets were dried at room temperature with occasional stirring to prevent matting. The average particle size was about 3 to 5 microns.

Example 2

To 100 grams of a blue-sensitive gelatino-silver bromoiodide emulsion of the same kind as used in Example 1 there was added with stirring at 40° C. a solution of the following resin coupler made by dissolving 1 gram of the coupler in a solution of 7 cc. of 0.5 N sodium hydroxide and 10 cc. of water.



This coupler is similar to that of Example 8 of U. S.

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Patent 2,698,797, but was made from vinyl acetate-maleic anhydride instead of styrene-maleic anhydride resin. The pH of the resulting emulsion was adjusted with citric acid to 6.1. The viscosity of this emulsion dropped during the reduction in pH and appeared to reach a minimum at 6.5. Solution could therefore be carried out at this pH.

Packets were then prepared by dispersing this emulsion in the same way as described in Example 1. Packets were obtained having an average size of 3 to 10 microns.

Example 3

A mixture of 1.5 grams of the resin coupler of Example 14 of U. S. Patent 2,698,797 and 10 cc. of 0.5 N sodium hydroxide were heated on a steam bath. When a moderately high viscosity was reached the dope was diluted with 10 cc. of water and the heating and stirring was continued until solution was complete. The pH of this solution after cooling to room temperature was then adjusted to 8.75. The total weight was 25 grams. 12.5 grams of this solution was added at 40° C. to 50 cc. of a green-sensitive gelatino-silver bromiodide emulsion of the same composition as that used in Example 1 and well stirred. There appeared to be little viscosity change. The pH was adjusted to 6.72 with 10% aqueous citric acid.

Packets were then prepared by adding the emulsion to mineral oil as described in Example 1 except that 1 cc. of chromic chloride solution (2 grains per cc.) was added in place of the mucochloric acid as a hardener. Packets were obtained having a particle size of 3 to 5 microns.

Example 4

The packet emulsions prepared as described in Examples 1 to 3 were mixed with gelatin and coated on film base to form a three-color, single-layer mixed packet dispersion.

Example 5

To 200 cc. of mineral oil at 45° containing diglycerol monolaurate was added 4 cc. of a solution of 2-vinylpyridine polymer metho-p-toluenesulfonate solution. The pH of the vinylpyridine polymer quaternary salt had previously been adjusted to 7.07 with 40% aqueous sodium hydroxide solution. The suspension was stirred for 3 minutes and then 20 cc. of the coupler dispersion described below was added at 40°. The packets were then hardened with mucochloric acid and then separated from the dispersion as described in Example 1. The packets thus obtained were slightly sticky and averaged about 5 microns in diameter.

The coupler dispersion was made by diluting 298 g. of a slow gelatino-silver bromiodide emulsion with 175 cc. of water and adding 48 cc. of coupler solution, and then adjusting the pH of the mixture to 6.5 with citric acid while stirring.

The coupler solution was made by mixing 8.3 g. of the magenta coupler 1-phenyl-3-[3-{2-(2,4-di-tert. amyphenoxy) - 4 - o - sulfobenzamido} - benzamido - benzamido]-5-pyrazolone, 20 cc. of ethyl alcohol, and 4.4 cc. of 20% sodium hydroxide solution, stirring the mixture at 104° F., and after 3-4 minutes adding 47 cc. of water, and stirring for a few minutes to give a clear solution of the coupler.

In using couplers of the type described in Example 5, mordants other than the polyvinyl pyridine quaternary salt may be used such as piperidyl cellulose, polyvinyl piperidine, chitosan, the polymeric biguanides, or N-alkyl-amino celluloses, e. g. N-n-butyl amino cellulose.

Packets made according to our invention may be used for black-and-white development by omitting the coupler from the packet.

The preparation of the resin couplers used according to our invention is described in Godowsky and Minsk U. S. Patent 2,698,797. Other resin couplers capable of forming a magenta image upon coupling are the pyrazo-

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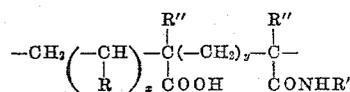
lyl styrene-maleic acid interpolymers described in Laakso and Allen U. S. Patent 2,646,421.

It will be understood that the examples included herein are illustrative only and that our invention is to be taken as limited only by the scope of the appended claims.

We claim:

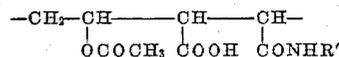
1. The method of making a packet photographic emulsion which comprises mixing with a gelatino-silver halide emulsion a water-soluble salt of a water-soluble coupler capable of reacting with the oxidation product of a primary aromatic amino developing agent on photographic development to form a dye and non-diffusing in photographic gelatin layers, to form a solution of said coupler in said emulsion, mixing said emulsion with a viscous hydrocarbon oil and forming a dispersion of said emulsion in said oil, adding a gelatin hardening agent to said dispersion to harden the dispersed emulsion particles, removing the dispersed particles from said oil and redispersing them in gelatin to form a dispersion of particles of gelatin, silver halide and coupler in a matrix or continuous phase of gelatin.

2. The method of making a packet photographic emulsion which comprises mixing with a gelatino-silver halide emulsion a water-soluble salt of a resin-coupler non-diffusing in photographic gelatin layers and having the recurring structure



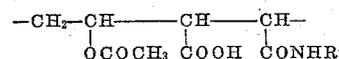
where R is selected from the class consisting of hydrogen, phenyl, alkyl, alkoxy, carboxyalkyl and acyloxy radicals, x and y are selected from the class consisting of 0 and 1, R' represents a color-forming group including an aryl group, capable of reacting with the oxidation product of a primary aromatic amino developing agent on photographic development to form a dye, and R'' is selected from the class consisting of hydrogen and an alkyl radical, to form a solution of said resin-coupler in said emulsion, mixing said emulsion with a viscous hydrocarbon oil and forming a dispersion of said emulsion in said oil, adding a gelatin hardening agent to said dispersion to harden the dispersed emulsion particles, removing the hardened emulsion particles from the dispersion, and redispersing said particles in gelatin to form a dispersion of particles of hardened gelatin, silver halide and resin-coupler in a matrix or continuous phase of gelatin.

3. The method of making a packet photographic emulsion which comprises mixing with a gelatino-silver halide emulsion a water-soluble salt of a resin-coupler of the recurring structure



where R' represents a color-forming group including an aryl group, capable of reacting with the oxidation product of a primary aromatic amino developing agent on photographic development to form a dye, thereby forming a solution of said resin-coupler in said emulsion, mixing said emulsion with a hydrophobic liquid and forming a dispersion of said emulsion in said liquid, adding a gelatin hardening agent to said dispersion to harden the dispersed emulsion particles, removing the hardening emulsion particles from the dispersion, and redispersing said particles in gelatin to form a dispersion of particles of hardened gelatin, silver halide and resin-coupler in a matrix or continuous phase of gelatin.

4. The method of making a packet photographic emulsion which comprises mixing with a gelatino-silver halide emulsion a water-soluble salt of a resin-coupler of the recurring structure



where R' represents a color-forming group including an

